Cycloaddition Reaction of Cycloheptatrienethione with Cyclopentadiene

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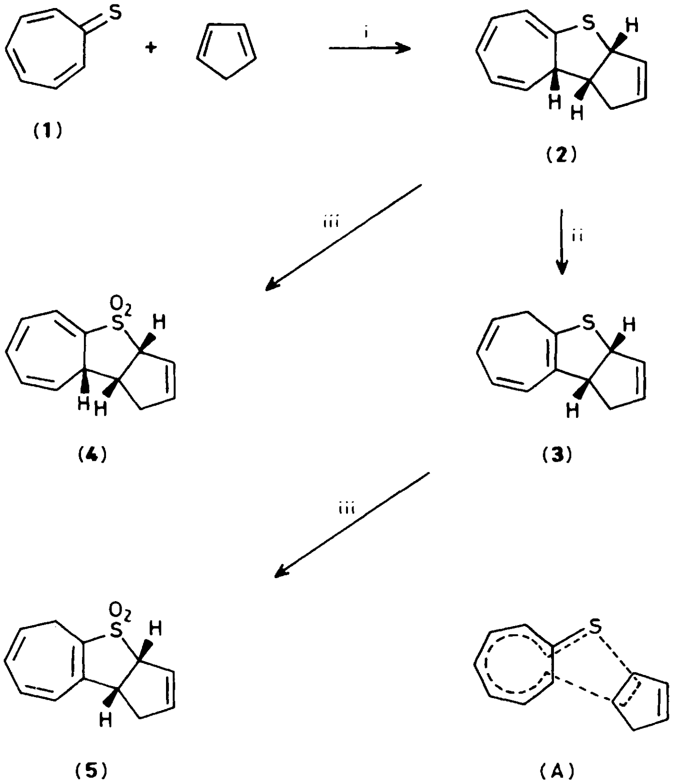
Cycloheptatrienethione, which is iso-π-electronic with tropone, reacts in a concerted manner with cyclopentadiene to give a 1 : 1 [8 + 2]-type adduct; the cyclopentadiene reacts as a 2π-component, in contrast with the case of tropone and the reaction mechanism is confirmed by a study of its kinetic behaviour.

We have recently reported[1] the synthesis and isolation of cycloheptatrienethione (**1**), the sulphur analogue of tropone as a thermally-unstable crystalline material differing sharply in its physical properties from tropone.[2] We now report that, whereas tropone gives a [6 + 4]-type adduct with cyclopentadiene,[3] cycloheptatrienethione, (**1**), gives an [8 + 2] adduct with high stereo- and regio-specificity.

To a freshly prepared solution of (**1**) cyclopentadiene in chloroform or dichloromethane was added at room temperature, and the reaction mixture was stirred under a nitrogen atmosphere for 3 h at 40 °C. Removal of the volatile material left a pale brown liquid. Purification gave an adduct (**2**) (pale yellow needles, m.p. 8.0–10.0 °C; b.p. 52 °C/0.10 mmHg, in 89% yield),† whose structure was determined by n.m.r. spectroscopy using the nuclear Overhauser effect, and by considering all the possible isomers of 1 : 1 adducts resulting from various combinations of (**1**) and cyclopentadiene.



Scheme 1. *Reagents and conditions:* i, $CHCl_3$, 40 °C; ii, toluene, reflux, or catalytic amount of CF_3CO_2H, room temp.; iii, monoperphthalic acid, $CHCl_3$, −6 °C.

The adduct (**2**) decomposes gradually when allowed to stand at room temperature, to form a new isomer (**3**).‡§¶ Both the products were oxidized, to aid the structural elucidation, with excess of monoperphthalic acid in chloroform at −6 °C to give the corresponding thermally stable sulphones (**4**) (71%) and (**5**) (86%), respectively.

A kinetic study of the cycloaddition reaction was carried out to establish the reaction mechanism at seven different temperatures in solvents with different polarities under pseudo first-order conditions. The molarity of cyclopentadiene was fixed at 20 times that of (**1**). The reaction was followed by a decrease in the intensity of the u.v. maximum of (**1**) at 380 nm.[2] The resulting activation parameters are listed in Table 1. The activation parameters agree closely with those for the cycloaddition of tropone with cyclopentadiene[3d] and the general values found for typical concerted cycloadditions.[4] The values strongly suggest that the reaction proceeds in a concerted manner through the highly oriented compact transition state of a 10π peripheral system (A). The configuration of the adduct (**2**) implies that the reaction proceeds in a

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† The absence of significant amounts of other products was demonstrated by h.p.l.c. analysis and ^1H n.m.r. spectroscopy during the reactions at 0, 10, 20, and 45 °C. When the adduct (**2**) was distilled at higher temperatures, partial conversion into (**3**) occurred.

‡ Satisfactory elemental analyses and spectral data were obtained for all new compounds. Spectroscopic data for (**2**), i.r. $\nu_{max.}$ (neat) 3010m, 2920m, 1580s, and 700vs cm^{-1}; u.v.-visible $\lambda_{max.}$ (EtOH) 239 (log ε 3.90) and 319 nm (3.58); mass *m/z* 188 (M^+, base), 123 (69), 122 (79), 121 (75), and 78 (58); ^1H n.m.r. (100 MHz, $CDCl_3$) δ 2.47—2.78 (3H, m) including signals at 2.60 (1H, ddt, *J* 8.8, 5.4, 1.0 Hz), 2.70 (2H, ddd, *J* 6.8, 4.9, 1.5 Hz), 3.32 (1H, dddd, *J* 8.8, 7.0, 6.8, 4.9 Hz), 4.75 (1H, dddt, *J* 7.1, 2.0, 1.7, 1.5 Hz), 4.98 (1H, dd, *J* 9.3, 5.4 Hz), 5.70 (1H, dddd, *J* 6.0, 2.2, 2.0, 1.7 Hz), 5.90 (1H, dddd, *J* 6.0, 2.2, 2.0, 1.5 Hz), 6.00—6.30 (2H, m), 6.38 (1H, ddd, *J* 5.9, 1.2, 1.0 Hz), and 6.51 (1H, ddd, *J* 10.2, 5.9, 1.0 Hz); ^{13}C n.m.r. (25.1 MHz, $CDCl_3$) δ 34.46 (t), 48.93 (d), 50.49 (d), 60.14 (d), 113.21 (d), 121.89 (d), 125.89 (d), 126.42 (d), 130.76 (d), 131.34 (d), 131.98 (d), and 140.46 (s).

§ *Selected spectroscopic data:* (**3**), pale yellow liquid, b.p. 85.0 °C/0.13 mmHg, i.r. $\nu_{max.}$ (neat) 750vs cm^{-1}; u.v.-visible $\lambda_{max.}$ (EtOH) 239 (log ε 3.67) and 329 nm (3.41); mass *m/z* 188 (M^+, base), 187 (66), 173 (45), 161 (47), 147 (43), and 128 (27); ^1H n.m.r. (90 MHz, $CDCl_3$) δ 2.41 (1H, dddd, *J* 16.5, 5.2, 2.7, 0.7 Hz), 2.41—2.76 (2H, m), 2.76 (1H, ddtd, *J* 16.5, 7.7, 2.3, 2.0 Hz), 3.93 (1H, ddddd, *J* 9.2, 7.7, 2.7, 1.7, 1.1 Hz), 4.75 (1H, ddt, *J* 9.2, 3.9, 2.0 Hz), 5.25 (1H, dtt, *J* 9.5, 6.9, 1.0 Hz), 5.52—5.85 (2H, m), 5.98 (1H, ddd, *J* 9.5, 4.0, 2.5 Hz), and 6.12—6.28 (2H, m); ^{13}C n.m.r. (22.5 MHz; $CDCl_3$) δ 28.23 (t), 39.34 (t), 53.04 (d), 57.16 (d), 120.33 (d), 127.33 (d), 127.40 (d), 127.87 (d), 128.60 (s), 130.44 (d), 131.36 (d), and 131.90 (s).

(**4**) Colourless prisms, m.p. 127.0—128.0 °C (MeOH), i.r. $\nu_{max.}$ (KBr) 1300vs and 1136vs cm^{-1}; mass *m/z* 220 (M^+, 2%), 156 (41), 141 (46), 128 (29), 115 (42), 91 (43), and 90 (base).

(**5**) Colourless prisms, m.p. 126.5—127.5 °C (MeOH), i.r. $\nu_{max.}$ (KBr) 1290vs and 1130vs cm^{-1}; mass *m/z* 220 (M^+, 14%), 156 (base), 155 (59), 141 (84), 128 (95), and 115 (63).

¶ A sample of the adduct (**2**) left for a week at room temperature showed an increase in the yield of (**3**) (58%) with a concurrent decrease of (**2**) (42%). Refluxing (**2**) in toluene overnight gave (**3**) in 53% yield. Similarly the rapid formation of (**3**) occurred in 48% yield when a small amount of trifluoroacetic acid was added into a reaction mixture.

Table 1. Activation parameters for the cycloaddition of cycloheptatrienethione with cyclopentadiene.

Solvent	Chloroform	Benzene
E_a[a]	11.7	11.5
$\log A$[b]	4.56	4.13
$\Delta S^{\ddagger}$[c]	−37.8	−39.6
$\Delta H^{\ddagger}$[a]	11.1	11.0
$\Delta G^{\ddagger}$[a]	22.8	23.2

[a] Units: kcal mol^{-1} (1 kcal = 4.184 kJ). [b] Units: s^{-1}. [c] Units. e.u. entropy unit = cal mol^{-1} K^{-1}.

suprafacial–suprafacial manner with *endo* approach. Hence, we can conclude that the formation of the cycloadduct (**2**) from the reaction of (**1**) with cyclopentadiene is a concerted $[_{\pi}8_s + _{\pi}2_s]$-type cycloaddition.||

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|| An SCF MO calculation has been reported for the molecule (**1**), which has the largest coefficients at the exocyclic terminal S and the C-2 positions in the HOMO.[5]

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